

U.S. DEPARTMENT OF COMMERCE  
National Technical Information Service

PB-270 965

# **A Study of New Catalytic Agents to Determine Chemical Oxygen Demand**

**Texas Southern Univ, Houston Dept. of Chemistry**

**Prepared for**

**Environmental Monitoring and Support Lab, Cincinnati, Ohio**

**May 77**

PB 270 965

PRODUCED BY  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U. S. DEPARTMENT OF COMMERCE

| TECHNICAL REPORT DATA<br>(Please read instructions on the reverse side of this form)                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                    |                                                       |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|-------------------------------------------------------|
| 1. REPORT NO.<br>EPA-600/4-77-038                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 2. RECIPIENT'S ACCESSION NO.                                                                       |                                                       |
| 3. TITLE AND SUBTITLE<br>A STUDY OF NEW CATALYTIC AGENTS TO DETERMINE CHEMICAL OXYGEN DEMAND                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 4. REPORT DATE<br>May 1977 (Issuing Date)                                                          | 5. PERFORMING ORGANIZATION CODE                       |
| 7. AUTHOR(S)<br>Ray F. Wilson                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 6. PERFORMING ORGANIZATION REPORT NO.                                                              |                                                       |
| 8. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Department of Chemistry<br>Texas Southern University<br>Houston, Texas 77004                                                                                                                                                                                                                                                                                                                                                                                                                       | 10. PROGRAM ELEMENT NO.<br>18A027 18A123                                                           | 11. CONTRACT/GRANT NO.<br>R803779-01                  |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Environmental Monitoring & Support Lab. - Cin., OH<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Cincinnati, OH 45268                                                                                                                                                                                                                                                                                                                                                | 13. TYPE OF REPORT AND PERIOD COVERED<br>7/20/76 - 12/30/77                                        |                                                       |
| 14. SUPPLEMENTARY NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 15. SPONSORING AGENCY CODE<br>EPA/600/06                                                           |                                                       |
| 16. ABSTRACT<br><br>This study was made to find a catalyst to replace silver sulfate in the COD method in order to reduce the cost of the determination. The results show that comparable results to the standard method for concentration of 50-500 mg/l could be obtained using a reduced amount of silver sulfate in combination with magnesium sulfate. Another procedure is described for determining COD in the range of 5-50 mg/l using a combination of silver sulfate, aluminum sulfate and magnesium sulfate to replace silver sulfate. |                                                                                                    |                                                       |
| 17. KEY WORDS AND DOCUMENT ANALYSIS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                    |                                                       |
| a. DESCRIPTORS<br><br>Magnesium sulfates<br>Water analysis                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | b. IDENTIFIERS/OPEN ENDED TERMS<br><br>Catalytic<br>Chemical oxygen demand (COD)<br>Silver Sulfate | c. SUBJECT Field/Group<br><br>07B                     |
| 18. DISTRIBUTION STATEMENT<br><br>Release to Public                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 19. SECURITY CLASS (This Report)<br>UNCLASSIFIED<br>20. SECURITY CLASS (This page)<br>UNCLASSIFIED | 21. NO. OF PAGES<br>79<br>22. PRICE<br>\$1.00 - \$2.1 |



EPA-600/4-77-038  
May 1977

**A STUDY OF NEW CATALYTIC AGENTS TO DETERMINE  
CHEMICAL OXYGEN DEMAND**

by

Ray F. Wilson  
Texas Southern University  
Houston, Texas 77004

Grant No. R80J779-01

Project Officer

Harris E. Gales, Jr.  
Environmental Monitoring and Support Laboratory  
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
CINCINNATI, OHIO 45268

#### DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- a Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- b Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- c Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

There is an ever-increasing interest in improving methods to analyze water and waste samples, whether the resulting data are to be used for research, surveillance, compliance monitoring, or enforcement purposes. Accordingly, the Environmental Monitoring and Support Laboratory has an on-going methods research effort in the development, evaluation, and modification of standard procedures. This particular report pertains to procedural modification for chemical oxygen demand measurement. The method has potential routine application for the analysis of chemical oxygen demand in surface waters and domestic and industrial wastes.

Dwight G. Ballinger  
Director  
Environmental Monitoring and Support Laboratory

## ABSTRACT

Of the several methods proposed for chemical oxygen demand (COD) determinations, the dichromate reflux method has generally been adopted as the standard procedure using silver sulfate as the catalyst. Inasmuch as silver sulfate is extremely expensive, the purpose of this study was to ascertain which of the nontoxic elements, iron, copper, zinc, aluminum, etc., could be employed for a substitute catalyst for silver sulfate in the procedure. The results obtained in this study show that among the catalysts investigated, silver sulfate is generally the best for carrying out COD determinations. However, substantially the same results could be obtained from samples in the high-level range of approximately 500 milligrams by using a reduced amount of silver sulfate in combination with magnesium sulfate.

A procedure is described for determining the COD values of solutions having sample concentrations in the range 5 to 50 milligrams. The method is a modification of the standard Moore procedure, in that a combination of silver sulfate, aluminum sulfate, and magnesium sulfate is used to replace the silver sulfate catalyst. This revised procedure is generally comparable in completeness of oxidation and is less expensive than the Moore procedure. Data are reported for pure synthetic organic samples and for certain bayou samples.

This report was submitted in fulfillment of Grant No. R803779-01 by Texas Southern University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 20, 1975, to December 20, 1977, and work was completed as of March 1, 1977.

## CONTENTS

|                                                                                                      |     |
|------------------------------------------------------------------------------------------------------|-----|
| Foreword                                                                                             | iii |
| Abstract                                                                                             | iv  |
| Acknowledgment                                                                                       | vii |
| 1. Introduction                                                                                      | 1   |
| 2. Conclusions                                                                                       | 2   |
| 3. Recommendations                                                                                   | 3   |
| 4. Experimental Procedures                                                                           | 4   |
| 5. Results and Discussion                                                                            | 7   |
| References                                                                                           | 11  |
| Appendices                                                                                           |     |
| 1. Effect of Silver Sulfate Using Moore Method for Determining Oxygen Consumed                       | 12  |
| 2. Effect of Different Volumes of Sulfuric Acid on COD Values Using 15 ml of Silver Sulfate Catalyst | 13  |
| 3. Effect of Different Substitute Catalysts for Silver Sulfate for Determining Oxygen Consumed       | 14  |
| 4. Effect of Different Combination Catalysts for Determining Oxygen Consumed                         | 16  |
| 5. Effect of Time of Heat on COD Values of Acetic Acid Using the Revised Moore Method                | 18  |
| 6. Comparison of Certain COD Values Using Revised Method Friedrich's Condenser Vs. Dry-Ice Condenser | 19  |
| 7. Carbon Content of Stock Sample Solutions Using Total Carbon Analyser                              | 20  |
| 8. Statistical Analysis for Acetic Acid Using 15 ml $\text{Ag}_2\text{SO}_4$ + 1gr $\text{MgSO}_4$   | 21  |
| 9. Effect of Silver Sulfate Using Moore Method for Determining Oxygen Consumed                       | 22  |

|     |                                                                                                     |    |
|-----|-----------------------------------------------------------------------------------------------------|----|
| 10. | Effect of Different Catalysts on COD Values for Different Organic Compound . . . . .                | 23 |
| 11. | Effect of Combinations Catalysts on COD Values for Different Organic Compounds . . . . .            | 24 |
| 12. | Effect of Silver Sulfate on COD Values in the Presence of Aluminum and Magnesium Sulfates . . . . . | 26 |
| 13. | The Effect of Different Catalyst or Catalyst Combinations on COD for Acetic Acid . . . . .          | 27 |
| 14. | Standard Method Vs. Revised Method Using Houston Area Water Samples . . . . .                       | 28 |

#### ACKNOWLEDGMENTS

The author wishes to extend sincere thanks to the personnel of the Environmental Monitoring and Support Laboratory, especially Mr. Morris E. Sales, Jr., for their invaluable assistance to the project. Also acknowledged is the assistance of George Witt, Hossamedin Ebrahimsadeh, Abdolkarim Ghafouripour, Mohammad Khorasani, Shahrrok Shirazi, and Patricia A. Smith for their help.

## SECTION I

### INTRODUCTION

Previously several methods have been proposed for determination of chemical oxygen demand (COD) values in certain waters and wastes. The dichromate reflux method (1) using silver sulfate as a catalyst is generally accepted as the standard procedure (2) for COD determinations. This method suffers from the fact that the availability of silver sulfate is low and the cost of this catalyst is extremely high, presently approximately \$400 per pound. In addition to the dichromate procedure, several other less well accepted methods have been proposed, e.g., the iodine method of Dayadze (3), later modified by Johnson, Halvorsen, and Tsuchiya (4), the permanganate method (5), the perchloratoceric acid procedure (6), and the elimination of chloride interference in the dichromate reflux COD test by Dobbs (7) and Williams and Baumann (8) by the addition of mercuric sulfate to form unionized mercuric chloride.

In attempting to control our environment, we frequently need to know the amount and extent of oxidation of organic matter in our water and waste systems. Thus, there is a need for an economical, sensitive, and rapid determination of oxygen required to oxidize the organic matter in waste samples. The low availability and high cost of silver sulfate catalyst employed in the standard COD procedure give rise to a need for finding a low-cost substitute catalyst. This study was undertaken, first, to ascertain which of the nontoxic elements (iron, nickel, copper, zinc, aluminum, etc.), may be used for a substitute or partial substitute catalyst for silver sulfate in the standard COD procedure and secondly, to evaluate the best replacement catalytic agent for COD determination, standardize the procedure, and test its validity.

This project was divided into two phases. Phase (I) was concerned with high level COD determinations and involved: (a) an evaluation of the effect of sulfuric acid on the completeness of oxidation, (b) effect of different proposed substitute catalysts, (c) effect of different combination catalysts, (d) effect of time of heating, and (e) a comparison of COD values using the Friedrich's condenser versus a dry ice condenser. In Phase (II), low level COD studies in the concentration range 5 to 50 milligrams per sample were carried out involving considerations similar to those for high level COD determinations.

## SECTION II

### CONCLUSIONS

This work has demonstrated

1. that among the catalysts studied, silver sulfate is generally the best catalyst for carry out COD determinations.
2. that in the high-level, revised COD procedure substantially the same COD values could be obtained using 15 ml of silver sulfate solution in combination with 1 magnesium sulfate instead of the 70 ml of silver sulfate solution required in the standard COD procedure.
3. that in the low-level, proposed procedure comparable results could be obtained by using 20 ml of silver sulfate solution in combination with 1 g aluminum sulfate and 1 g magnesium sulfate instead of the 70 ml of silver sulfate solution required in the standard procedure.
4. that the data obtained using the standard method vs. the revised method for measuring COD values of real water samples showed that the revised method is comparable to the standard method.

Preliminary work indicated that the COD values for certain extremely volatile organic compounds could be materially increased by using a dry ice condenser filled with crushed ice instead of a Friedrich's condenser. These studies suggest that further studies using a dry ice or modified dry ice condenser are desirable.

### SECTION III

#### RECOMMENDATIONS

1. In this study the Friedrich's reflux condenser was generally employed; however, a limited number of determinations were carried out using a dry ice condenser. The COD values for certain volatile compounds was substantially higher when a dry ice condenser filled with crushed ice was used. Thus more studies should be carried out using a dry ice condenser.
2. Further studies should be carried out using a dry ice condenser filled with different freezing point mixtures.
3. It is recommended that further studies be carried out on the variables such as time of heating and temperature of refluxing medium using a dry ice or modified dry ice condenser.
4. It is recommended that the silver sulfate-magnesium sulfate-aluminum sulfate catalyst replace the silver sulfate catalyst in the Standard Chemical Oxygen Demand Method.

## SECTION IV

### EXPERIMENTAL PROCEDURES

#### APPARATUS

Each reflux apparatus used consisted of a pyrex 500 ml round bottom or Erlenmeyer flask fitted with a 24/40 taper-joint neck connected with a Friedrich's reflux condenser or a dry ice condenser, in designated cases, in which crushed ice was used. Standard hot plates were employed to heat the reflux solutions. All samples, unless otherwise indicated, were run in triplicate, simultaneously with a blank containing 50 ml of deionized water.

A total organic carbon analyzer, model DC-30, obtained from the Bohrmann Division, Division of Envirotech Corporation, Mountain View, California, was used to verify the carbon content in the COD samples used in this study. This instrument was standardized before each series of determinations against reagent grade potassium hydrogen phthalate dissolved in deionized water.

#### REAGENTS AND SOLUTIONS

All solutions were prepared from reagent grade chemicals. For high-level range COD determinations (approximate range of 300 mg of sample per liter), standard potassium dichromate, 0.250 N, was prepared by dissolving 12.2588 g of dried  $K_2Cr_2O_7$  in a 1 liter flask and diluting the solution to volume. Sulfuric acid<sup>2</sup> containing 23.5 g of silver sulfate per 9 lb bottle was employed after allowing two days for complete dissolution. Phenanthroline ferrous sulfate (Ferrion) indicator solution was prepared by dissolving 98 g of 1-10 (ortho) phenanthroline monohydrate and 0.70 g of  $FeSO_4 \cdot 7H_2O$ . Standard ferrous ammonium sulfate, approximately 0.250 N was prepared by dissolving 98 g of  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  in deionized water, then adding 20 ml of concentrated sulfuric acid, cooling, and diluting the solution to a volume of 1 l. The standard ferrous ammonium sulfate was standardized daily as its concentration decreases on standing.

Standard reagent solutions for low level COD determinations were prepared as described above for the high level procedure, except the solutions were made one-tenth the concentrations used in the high-level procedure. For bayou samples which contained chlorides, mercuric sulfate was added to the digestion flask to complex the chlorides, thus eliminating the chloride interference, except for samples which contained a very high chloride and required a chloride correction (2).

## CALCULATIONS

1. Theoretical COD: A typical theoretically calculated COD, mg/l, for acetic acid is presented using the following balanced equation



The theoretical COD in this case for a 300 mg sample of acetic acid is:

$$\text{COD, mg/l} = 300 \frac{\text{mg of HC}_2\text{H}_3\text{O}_2}{1} \times \frac{64 \text{ mg of O}_2/2 \text{ moles}}{60 \text{ mg of HC}_2\text{H}_3\text{O}_2/\text{mole}} = 333 \frac{\text{mg of O}_2}{1}$$

2. Experimental COD value: The experimental COD values reported in this study are expressed in mg/l using the following equation:

$$\text{mg/l COD} = \frac{(A - B)C \times 8,000}{\text{ml sample}}$$

where: COD = Chemical Oxygen Demand, mg/l of sample

A = ml of ferrous ammonium sulfate used for blank

B = ml of ferrous ammonium sulfate used for sample

C = the normality of ferrous ammonium sulfate.

## RECOMMENDED REVISED MOORE HIGH LEVEL COD PROCEDURE

Several boiling stones are placed in a reflux flask which has been placed in an ice bath. To this flask is added 25 ml of potassium dichromate solution, 15 ml of silver sulfate solution (23.5 g of silver sulfate per 9-16 bottle of conc. sulfuric acid) plus one gram magnesium sulfate. While swirling the resulting solution, 55 ml of concentrated sulfuric acid and 50 ml of a test COD sample which contained an accurately known amount of compound ranging from approximately 250 to 500 mg of sample per liter are added to the mixture in the reflux flask. After this solution is refluxed for two hours, the flask is allowed to cool, and the inside of the condenser is washed with 25 ml of deionized water. Ten drops of ferrion indicator are added to the solution at room temperature and the excess potassium dichromate is titrated with 0.25 N ferrous ammonium sulfate to the ferrion end point, where the solution changes from blue green to reddish brown. The COD values of the aromatic hydrocarbons are increased markedly by substituting a dry ice cooled condenser, filled with crushed ice (frozen water), in place of a Friedrich's condenser.

#### RECOMMENDED REVISED MOORE LOW LEVEL COD PROCEDURE

Several boiling stones are placed in a reflux flask which has been placed in an ice bath. To this flask is added 25 ml of potassium dichromate, 20 ml of silver sulfate solution (25.5 g of silver sulfate per 9-1b bottle of conc. sulfuric acid) plus one gram magnesium sulfate and one gram aluminum sulfate. While swirling the resulting solution, 50 ml of concentrated sulfuric acid and 50 ml of a test COD sample which contained an accurately known amount of compound ranging from approximately 5 to 50 mg of sample per liter are added to the mixture in the reflux flask. After this solution is refluxed for two hours, the flask is allowed to cool, and the inside of the condenser is washed with 25 ml of deionized water. Ten drops of ferrion indicator are added to the solution at room temperature and the excess potassium dichromate is titrated with 0.025 N ferrous ammonium sulfate the ferrion end point.

## SECTION V

### RESULTS AND DISCUSSION

#### PHASE I

The first part of this study consisted of evaluating the COD values of ten selected organic compounds by using various amounts of silver sulfate solution (23.9 g Ag<sub>2</sub>SO<sub>4</sub> per 9 oz bottle) as a catalyst. The concentration effect of silver sulfate as a catalyst was ascertained by determining the COD values for each of ten selected compounds in the presence of 5, 10, 15, 20, 35, 50, 70 ml of the silver sulfate solution. The organic compounds selected represent different classes of organic substances that may be found in wastewater. A solution of each of the ten organic compounds was prepared by dissolving approximately 500 mg of each in 100 ml of de-ionized water and diluting to 1000 ml. The results of the oxidation of these compounds are shown in Table 1. According to these tabular data acetic acid and ethyl alcohol gave essentially the same results in the presence of 15 ml of silver sulfate solution as the 70 ml recommended in the standard procedure. These results suggest that using 15 ml of silver sulfate solution gives substantially the same catalytic effect as 70 ml. Such reduction in the required amount of silver sulfate catalyst gives rise to approximately a 4-fold reduction in the cost of running a COD determination because of the materially high cost of silver sulfate.

The effect of sulfuric acid concentration on typical COD values obtained using the standard Moore COD procedure is shown in Table 2. These results show that high-percentage results are generally obtained with high sulfuric acid concentrations. For the compounds studied, that are almost completely oxidized by 15 ml of silver sulfate solution plus 55 ml of sulfuric acid, significantly lower COD values were obtained at very low sulfuric concentrations.

In the third part of this study 16 suggested substitute catalysts were employed to obtain chemical oxygen demand values for the same organic compounds which were used in the first step. It should be emphasized that, although used for this study, none of these individual catalysts could be used as a replacement for silver sulfate giving the same completeness of oxidation of the compounds studied as are shown in Table 3. These data, however, do indicate that several of the catalysts do give high COD values for certain of the high molecular weight organic compounds.

The various combination of different catalysts such as

- 1" 1 g  $\text{Fe}_2(\text{SO}_4)_3$  + 1 g  $\text{Al}_2(\text{SO}_4)_3$
- 2" 1 g  $\text{Al}_2(\text{SO}_4)_3$  + 1 g  $\text{HgSO}_4$
- 3" 1 g  $\text{Fe}_2(\text{SO}_4)_3$  + 1 g  $\text{HgSO}_4$
- 4" 1 g  $\text{HgSO}_4$  + 15 ml  $\text{Ag}_2\text{SO}_4$  solution
- 5" 1 g  $\text{Al}_2(\text{SO}_4)_3$  + 15 ml  $\text{Ag}_2\text{SO}_4$  solution
- 6" 1 g  $\text{Fe}_2(\text{SO}_4)_3$  + 15 ml  $\text{Ag}_2\text{SO}_4$  solution
- 7" 1 g  $\text{HgSO}_4$  + 1 g  $\text{Al}_2(\text{SO}_4)_3$  + 15 ml  $\text{Ag}_2\text{SO}_4$  solution
- 8" 1 g  $\text{HgSO}_4$  + 1 g  $\text{Fe}_2(\text{SO}_4)_3$  + 15 ml  $\text{Ag}_2\text{SO}_4$  solution
- 9" 1 g  $\text{Fe}_2(\text{SO}_4)_3$  + 1 g  $\text{Al}_2(\text{SO}_4)_3$  + 15 ml  $\text{Ag}_2\text{SO}_4$  solution

were used in the last step. The evaluation of the above catalysts with the ten different organic compounds showed that 15 ml of silver sulfate solution in combination with  $\text{HgSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ , or  $\text{Fe}_2(\text{SO}_4)_3$  gave reasonable higher COD values as compared to the first three combination catalysts as shown in Table 4. The data in Table 4 indicate that comparable COD values are obtained for most of the above ten compounds when 15 ml of silver sulfate solution plus one gram of  $\text{HgSO}_4$ , are used to replace the 70 ml of silver sulfate solution required as the catalyst in the standard COD procedure. The magnesium sulfate-silver sulfate suggested replacement catalyst combination for silver sulfate does not substantially oxidize pyridine or aromatic hydrocarbons. These results are similar to one obtained using 70 ml of silver sulfate solution in the standard procedure. However, preliminary studies, Table 5, indicated that the COD values for aromatic hydrocarbons are materially increased by substituting a dry ice cooled condenser filled with crushed ice in place of a Friedrich's condenser. The selection of the best possible cooling mixture for a dry ice condenser in COD determinations should justify further study.

The results of the oxidation of these compounds showed that formaldehyde is oxidized by 74% when 70 ml of silver sulfate solution is used and 69% when 15 ml of silver sulfate solution is used in the standard procedure, acetic acid is 99% oxidized and 92% oxidized when 15 ml of silver sulfate solution is used as a catalyst (see in Table 1).

For high molecular weight organic compounds, viz., toluene, oleic acid, benzene, certain of the new catalysts gave higher oxidation values than 70 ml of silver sulfate solution. For example, toluene is oxidized by ferric oxide (70.3%), and benzene is oxidized by aluminum sulfate (36.7%), whereas silver sulfate gave respective oxidation values of 36.1%, 32.2%, 37.6% for toluene, oleic acid, and benzene (see Table 3).

Tabular data for effect of time of heating on COD values of acetic acid are shown in Table 5. Typical data were obtained for other compounds that are readily oxidized in boiling dichromate sulfuric acid solution, which indicate that such compounds are generally and substantially oxidized within the recommended 2-hour digestion period.

Typical data of the carbon content of stock sample solutions using the total carbon analyzer described above under Apparatus are reported in Table 7. These measurements were carried out to verify and test the comparative accuracy of the revised procedure.

Statistical treatment of certain data obtained in this study was carried out as described by Laitinen and Harris (9). Eleven replicate measurements of COD values for acetic acid, reported in Table 8 using the revised method proposed in this study gave a mean of 489 with a standard deviation of two COD units. The 95% confidence interval of the mean and the standard deviation are 489  $\pm$  2 and 1 to 3, respectively.

The data obtained in this phase of the study show that among the catalysts studied, silver sulfate is generally the best catalyst for carrying out COD determinations. However, substantially the same results could be obtained using 15 ml of silver sulfate solution in combination with 1 g magnesium sulfate. Thus, based on the data obtained in this study, the already described procedure is proposed for carrying out chemical oxygen demand determinations in the high level concentration range, thereby obtaining essentially the same COD values as those of the standard Moore method at less expense.

#### PHASE II

Inasmuch as the Moore method using silver sulfate as a catalyst has generally been accepted as a standard method for carrying out COD determinations, this procedure was selected for the studies reported herein. The primary emphasis in this study was to find a recommended replacement catalyst in the low level COD range of 5 to 50 mg of sample, for silver sulfate because of the extremely high cost of this catalyst.

The concentration effect of silver sulfate catalyst using the standard Moore method on eleven different organic compounds that might be found in certain wastes are shown in Table 9. These tabular data indicate that 20 ml of silver sulfate solution gives COD values fairly close to the ones obtained for 70 ml of silver sulfate solution for most of the compounds. Based upon exploratory tests, the 3 catalysts ( $\text{HgSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ , and  $\text{ZrOSO}_4$ ) were selected for detail study using eleven organic substances. These studies were carried out by placing accurately weighed samples of approximately 50 mg of each organic compound in separate 1 liter volumetric flasks and diluting the volume with deionized water. The data for these studies are shown in Table 10. Among the catalysts employed,  $\text{HgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  generally gave fairly high COD values; however, none of the 3 catalysts were effective in oxidizing acetic acid.

In an attempt to ascertain the additive catalytic effect of the aforementioned 3 selected catalysts, these catalysts were grouped in pairs giving rise to ten possible combinations. The pair combination catalytic effect of these catalysts are shown in Table 2. The  $\text{HgSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  generally gave the highest COD values.

The effect of silver sulfate concentration on COD values in the presence of one gram each of aluminum sulfate and magnesium sulfate are reported in Table 12. Correlation of these tabular data with the ones reported in Table 9, with the exception of acetic acid, show that 20 ml of silver sulfate solution in combination with aluminum sulfate and magnesium sulfate generally gave COD values fairly comparable to the ones obtained using 70 ml of silver sulfate solution.

Tabular data reported in Table 13 for true samples taken from selective sites locations in the Houston Ship Channel and adjoining wastewaters show that the COD values obtained using the revised procedure proposed in this study are comparable to the one determined using the standard procedure.

# REFERENCES

1. Moore, W. Allan, F. L. Ludsack, G. C. Buchhoff. Determination of Oxygen Consumed Values of Organic Wastes. *Analytical Chemistry*, 23, p 1297, 1951.
2. Methods for Chemical Analysis of Water and Wastes, EPA-625/6-74-003, Method Development and Quality Assurance Research Laboratory, National Environmental Research Center, U.S. Environmental Protection Agency, Office of Technology Transfer, Washington, D. C. 20460, 1974.
3. Dzyusio, A. M., Vodonashchenis i sanit. Tekh., No. 8-9, pp 117-22, 1938.
4. Johnson, F. W., H. O. Halvorsen, and H. M. Tauchiya. Abstracts of 109th meeting, American Chemical Society, Atlantic City, p 25, 1946.
5. Standard Methods for the Examination of Water and Sewage, 9th edition, American Public Health Association, New York, 1946.
6. Pitt, W. W., E. Kats, and L. H. Thacker. A Rapid Sensitive Method for the Determination of COD in Polluted Waters. *Water Aiche Series*, pp 1-5, 1972.
7. Dobbs, R. A., and R. T. Williams. Elimination of Chloride Interferences in the Chemical Oxygen Demand Test. *Analytical Chemistry*, 35, p 1064, 1963.
8. Bauman, F. J. Dichromate Reflux Chemical Oxygen Demand. A Proposed Method for Chloride Correction in Highly Saline Wastes. *Analytical Chemistry* 46, p 1336, 1974.
9. Laitinen, H. A., and W. E. Harris. *Chemical Analysis*, 2nd Edition, McGraw-Hill Book Company, New York, pp 540-541, 1960.

TABLE 1. EFFECT OF SOLVENT SOLUBILITY USING MORE SOLVENT FOR  
MECHANICAL MIXING CONTAINER

| Volume of Solvent Solution<br>ml (g of Benzene) |           |           |            |           |           |           |           |           |           |  |
|-------------------------------------------------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|--|
| Compounds                                       | 0         | 5         | 10         | 15        | 20        | 25        | 30        | 35        | 40        |  |
| Acetic acid                                     | 36.0(8.8) | 366(88.3) | 436(81.8)  | 480(71.9) | 528(86.0) | 530(86.4) | 530(86.8) | 530(86.8) | 530(86.8) |  |
| Benzene                                         | 37.8(2.5) | 98.0(8.4) | 208(13.5)  | 304(19.8) | 385(12.0) | 43.3(5.3) | 43.3(5.3) | 43.3(5.3) | 43.3(5.3) |  |
| tert-Butyl alcohol                              | 213(36.4) | 467(72.0) | 542(83.6)  | 571(88.0) | 584(88.0) | 607(83.6) | 615(85.0) | 615(85.0) | 615(85.0) |  |
| Ethyl alcohol                                   | 346(13.2) | 638(64.3) | 1529(72.7) | 824(79.0) | 867(85.0) | 842(86.3) | 950(81.2) | 946(81.7) | 946(81.7) |  |
| Formaldehyde                                    | 308(57.8) | 331(62.1) | 347(65.1)  | 370(68.4) | 311(58.5) | 293(55.0) | 300(56.3) | 306(54.3) | 306(54.3) |  |
| 1-Hydroxy-pyridine                              | 844(37.1) | 946(42.5) | 838(36.9)  | 834(36.7) | 954(42.0) | 954(42.0) | 952(41.9) | 946(37.2) | 946(37.2) |  |
| Glaic acid                                      | 141(19.5) | 174(26.1) | 204(28.6)  | 209(40.0) | 362(50.0) | 362(50.0) | 362(50.0) | 362(50.0) | 362(50.0) |  |
| Pyridine                                        | -         | 10.0(0.7) | 10.0(0.7)  | 10.0(0.7) | 15.0(1.0) | 15.0(1.0) | 15.0(1.0) | 15.0(1.0) | 15.0(1.0) |  |
| Sucrose                                         | -         | 538(99.6) | 538(99.6)  | 538(99.6) | 538(99.6) | 538(99.6) | 538(99.6) | 538(99.6) | 538(99.6) |  |
| Toluene                                         | 427(17.3) | 344(15.6) | 362(16.7)  | 386(19.6) | 346(15.7) | 311(13.5) | 305(11.8) | 305(11.8) | 305(11.8) |  |

TABLE 1. EFFECT OF DIFFERENT VOLUMES OF SULFURIC ACID ON CDS VALUES  
USING 15 ml OF SULFUR SULFONIC CATALYST

| Compounds          | Volume of $H_2SO_4$ , ml |           |           |           |           |
|--------------------|--------------------------|-----------|-----------|-----------|-----------|
|                    | 10                       | 20        | 30        | 40        | 55        |
| Acetic acid        | 304(57.8)                | 324(60.8) | 352(66.4) | 364(68.3) | 400(76.4) |
| Benzene            | 52( 6.8)                 | 140( 9.6) | 360(23.6) | 450(29.2) | 504(33.8) |
| tert-Butyl alcohol | 224(34.5)                | 300(39.8) | 386(51.1) | 460(72.2) | 570(88.0) |
| Ethyl alcohol      | 356(34.1)                | 352(33.7) | 352(33.7) | 360( 4.5) | 824(78.0) |
| Formaldehyde       | 360(60.0)                | 300(71.3) | 372(68.8) | 376(70.5) | 370(88.4) |
| 3-Hydroxypropylene | 704(34.5)                | 360(34.7) | 800(35.5) | 844(37.1) | 834(36.7) |
| Lactic acid        | 220(41.3)                | 200(39.0) | 236(44.3) | 256(48.0) | 460(56.0) |
| Maleic acid        | 20( 3.9)                 | 36( 5.0)  | 180(34.9) | 215(28.7) | 260(40.0) |
| Sucrose            | 504(60.8)                | 526(62.0) | 524(63.6) | 520(56.1) | 526(60.8) |
| Toluene            | 60( 3.0)                 | 153( 9.0) | 360(24.3) | 470(30.0) | 506(25.6) |

Each CDS value was calculated from triglyceride determinations

TABLE 1. EFFECT OF DIFFERENT SUBSTRATE CATALYSTS FOR SUGAR  
SULFATE FOR DEMONSTRATING DECOLORED

| Catalyst <sup>a</sup> | TIME       | 100 Values, %/l. (2 of Recovery) |                                 |                                 |                                 | M <sub>2</sub> (30.1) |
|-----------------------|------------|----------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------------|
|                       |            | Ag <sub>2</sub> SO <sub>4</sub>  | Ag <sub>2</sub> SO <sub>4</sub> | Ag <sub>2</sub> SO <sub>4</sub> | Ag <sub>2</sub> SO <sub>4</sub> |                       |
| <u>Compounds</u>      |            |                                  |                                 |                                 |                                 |                       |
| Acetic acid           | 36.0(16.8) | 520(37.5)                        | 27.9(5.2)                       | 27.9(5.2)                       | 15.9(6.7)                       | 69.7(13.1)            |
| Benzene               | 37.7(2.5)  | 578(37.6)                        | 74.8(4.9)                       | 257(26.7)                       | 122(7.9)                        | 154(10.8)             |
| tert-butyl alcohol    | 646(68.8)  | 646(39.6)                        | 672(71.8)                       | 644(68.5)                       | 666(71.5)                       | 686(76.5)             |
| ethyl alcohol         | 746(33.2)  | 936(39.7)                        | 560(53.7)                       | 574(14.7)                       | 556(53.3)                       | 580(53.7)             |
| Formaldehyde          | 308(57.8)  | 396(74.3)                        | 387(71.5)                       | 382(71.5)                       | 380(77.8)                       | 369(59.2)             |
| 3-hydroxypyridine     | 842(86.9)  | 847(87.5)                        | 846(87.4)                       | 852(88.1)                       | 840(87.8)                       | 988(102)              |
| Glacial acid          | 143(19.8)  | 213(32.2)                        | 246(34.8)                       | 210(29.8)                       | 236(34.1)                       | 688(84.7)             |
| Pyridine              | -          | -                                | -                               | -                               | -                               | -                     |
| Sucrose               | 522(98.7)  | 532(95.8)                        | 540(96.8)                       | 552(100)                        | -                               | 572(107)              |
| Toluene               | 622(31.4)  | 596(38.1)                        | 772(48.3)                       | 756(48.3)                       | 294(38.8)                       | 382(38.8)             |

TABLE 3 (continued)

| Catalysts<br>(Supplements) | GDS Values, mg/l. (G of Recovery) |            |                |            |            |            |
|----------------------------|-----------------------------------|------------|----------------|------------|------------|------------|
|                            | $Pb_2$                            | $Mn_2$     | $Al_2(SO_4)_3$ | $CuO$      | $CaSO_4$   |            |
| Acetic acid                | 43.9(18.2)                        | 35.9(16.7) | 38.8(7.5)      | 48.8(9.3)  | 8.0(1.5)   | 43.5(8.2)  |
| Benzene                    | 43.6(17.8)                        | 38.4(19.8) | 58.6(18.7)     | 78.4(5.2)  | 28.8(1.8)  | 48.6(26.3) |
| tert-Butyl alcohol         | 51.1(18.4)                        | 40.8(11.2) | 62.0(16.7)     | 43.9(14.6) | 40.8(13.8) | 50.6(12.9) |
| Butyl alcohol              | 56.7(14.3)                        | 43.8(13.7) | 60.0(7.5)      | 58.4(14.8) | 40.8(13.3) | 38.6(14.4) |
| Formaldehyde               | 38.0(17.7)                        | 37.6(18.5) | 3.62(16.7)     | 38.0(11.3) | 37.4(16.2) | 38.6(17.4) |
| 3-Hydroxypropylene         | 84.3(17.1)                        | 78.7(12.3) | 84.0(16.7)     | 98.8(10.2) | 83.6(15.3) | 95.7(14.8) |
| Maleic acid                | 57.5(19.5)                        | 27.4(17.9) | 42.1(18.1)     | 28.9(26.1) | 38.2(16.7) | 27.4(16.8) |
| Pyridine                   | -                                 | -          | -              | -          | -          | -          |
| Sucrose                    | 25.6(18.0)                        | 30.8(16.4) | 50.8(10.2)     | -          | 50.8(16.8) | 50.8(17.7) |
| Toluene                    | 28.2(11.7)                        | -          | 13.0(8.4)      | 48.8(19.4) | 78.2(5.8)  | 88.4(5.7)  |

\*In Tables IIIa, IIIb and IIIc, recovery efficiencies of Ag<sub>2</sub>SO<sub>4</sub> solutions or in the other cases 1 gram of the specific catalyst was used, except that only 0.1 gram of any platinum element compound was employed.

TABLE A. EFFECT OF DIFFERENT COMBUSTION CATALYSTS  
ON MEASURING SECOND COMBUSTION

| Compounds           | CIB Values, mg/l. (2 of Recovery)                                            |                                              |                                              |                                                           |
|---------------------|------------------------------------------------------------------------------|----------------------------------------------|----------------------------------------------|-----------------------------------------------------------|
|                     | $\text{Fe}_2(\text{SO}_4)_3 + \text{HgSO}_4$<br>$\text{As}_2(\text{SO}_4)_3$ | $\text{HgSO}_4 + \text{Fe}_2(\text{SO}_4)_3$ | $\text{HgSO}_4 + \text{Fe}_2(\text{SO}_4)_3$ | $\text{HgSO}_4 +$<br>1.5 ml. $\text{As}_2(\text{SO}_4)_3$ |
| Acetic acid         | 23.8(4.5)                                                                    | 59.5(11.2)                                   | 71.4(13.4)                                   | 53.6(96.4)                                                |
| Benzene             | 32.7(28.6)                                                                   | 440(29.9)                                    | 339(22.0)                                    | 603(29.2)                                                 |
| Tri-n-butyl alcohol | 385(88.9)                                                                    | 532(102.0)                                   | 442(68.1)                                    | 608(93.7)                                                 |
| Diethyl alcohol:1   | 325(38.1)                                                                    | 331(31.7)                                    | 363(34.8)                                    | 1,017(97.5)                                               |
| Benzaldehyde        | 32.3(82.6)                                                                   | 532(99.8)                                    | 385(72.2)                                    | 425(76.0)                                                 |
| 3-Dehydroxyproline  | 61.9(84.6)                                                                   | 835(109.3)                                   | 887(91.6)                                    | 857(82.5)                                                 |
| Gluolic acid        | 6.2(87.2)                                                                    | 675(93.3)                                    | 427(57.6)                                    | -                                                         |
| Pyridine            | 6.0(10.5)                                                                    | 29.8(2.4)                                    | 37.7(3.0)                                    | 43.6(3.6)                                                 |
| Sucrose             | 52.6(90.8)                                                                   | 552(98.6)                                    | 561(100)                                     | 182(11.6)                                                 |

TABLE 6 (continued)

| Compound            | 150 Volume <sup>a</sup> , 10/1 (2 of Reagents)                                                                                                                                                                                                       |                                                                                                                            |                                                               |                                                                                                                            |
|---------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
|                     | $\text{H}_2(\text{SO}_4)_3 + \text{H}_2(\text{SO}_4)_3 + \text{H}_2(\text{SO}_4)_3 + \text{H}_2(\text{SO}_4)_3$<br>15 ml. $\text{H}_2\text{SO}_4$ , 15 ml. $\text{H}_2\text{SO}_4$ , 15 ml. $\text{H}_2\text{SO}_4$ , 15 ml. $\text{H}_2\text{SO}_4$ | $\text{H}_2(\text{SO}_4)_3 + \text{H}_2(\text{SO}_4)_3$<br>15 ml. $\text{H}_2\text{SO}_4$ , 15 ml. $\text{H}_2\text{SO}_4$ | $\text{H}_2(\text{SO}_4)_3$<br>15 ml. $\text{H}_2\text{SO}_4$ | $\text{H}_2(\text{SO}_4)_3 + \text{H}_2(\text{SO}_4)_3$<br>15 ml. $\text{H}_2\text{SO}_4$ , 15 ml. $\text{H}_2\text{SO}_4$ |
| Acetic acid         | 666(33.3)                                                                                                                                                                                                                                            | 660(32.6)                                                                                                                  | 676(38.5)                                                     | 676(38.3)                                                                                                                  |
| Benzene             | 577(37.9)                                                                                                                                                                                                                                            | 567(36.9)                                                                                                                  | 672(43.7)                                                     | 669(38.5)                                                                                                                  |
| tert-Butyl Alcohol  | 573(38.3)                                                                                                                                                                                                                                            | 566(36.3)                                                                                                                  | 583(38.4)                                                     | 576(36.8)                                                                                                                  |
| Ethyl Alcohol       | 903(38.4)                                                                                                                                                                                                                                            | 896(37.3)                                                                                                                  | 913(37.5)                                                     | 922(38.2)                                                                                                                  |
| Bromobenzene        | 373(36.8)                                                                                                                                                                                                                                            | 371(36.6)                                                                                                                  | 383(38.5)                                                     | 374(36.5)                                                                                                                  |
| 3-Hydroxypropylene  | 752(37.7)                                                                                                                                                                                                                                            | 954(38.5)                                                                                                                  | 838(36.5)                                                     | 836(36.3)                                                                                                                  |
| Glacial acetic acid | -                                                                                                                                                                                                                                                    | -                                                                                                                          | 666(36.6)                                                     | 576(36.5)                                                                                                                  |
| Pyridine            | 19.8(3.4)                                                                                                                                                                                                                                            | 15.9(3.1)                                                                                                                  | 37.7(2.6)                                                     | 38.7(2.7)                                                                                                                  |
| Benzene             | -                                                                                                                                                                                                                                                    | 556(39.8)                                                                                                                  | 553(38.6)                                                     | 515(38.9)                                                                                                                  |
| Toluene             | 103( 9.1)                                                                                                                                                                                                                                            | 785( 6.7)                                                                                                                  | 102(10.4)                                                     | 156( 7.7)                                                                                                                  |

<sup>a</sup>On each case one gram of each catalyst plus 15 ml. of  $\text{H}_2\text{SO}_4$ . Reaction was run at 4.

TABLE 5. EFFECT OF TIME OF HEAT ON COD VALUES OF ACETIC ACID  
USING THE REVISED MOORE METHOD

| Time, Minutes              | Mean COD* Value, mg/l | % of Recovery |
|----------------------------|-----------------------|---------------|
| 1) After 30 Minute Shaking | 20.0                  | 3.8           |
| 2) Before Boiling Point    | 68.0                  | 12.8          |
| 3) 5 Minute After Boiling  | 236                   | 44.3          |
| 4) 10 " " "                | 244                   | 45.8          |
| 5) 15 " " "                | 300                   | 56.3          |
| 6) 20 " " "                | 316                   | 59.3          |
| 7) 25 " " "                | 328                   | 61.5          |
| 8) 30 " " "                | 340                   | 63.8          |
| 9) 35 " " "                | 412                   | 77.3          |
| 10) 40 " " "               | 448                   | 84.0          |
| 11) 60 " " "               | 460                   | 86.3          |
| 12) 80 " " "               | 476                   | 89.3          |
| 13) 100 " " "              | 496                   | 93.0          |
| 14) 140 " " "              | 504                   | 94.5          |
| 15) 180 " " "              | 504                   | 94.5          |
| 16) 220 " " "              | 508                   | 95.3          |
| 17) 340 " " "              | 508                   | 95.3          |

\*Mean COD values were determined from triplicate determinations using the recommended revised Moore procedure.

TABLE 6. COMPARISON OF CERTAIN COD VALUES USING REVISED METHOD  
FRIEDRICH'S CONDENSER VS. DRY-ICE CONDENSER

| Compound              | Mean COD,** mg/l | Mean COD* Value, mg/l(%) |
|-----------------------|------------------|--------------------------|
| 1) Sodium Stearate*** | 604(44.9)        | 792(58.8)                |
| 2) Glutamic Acid      | 448(76.4)        | 460(80.9)                |
| 3) Isobutyric Acid    | 592(65.1)        | 888(97.7)                |
| 4) Acetic Acid        | 490(91.9)        | 500(93.8)                |
| 5) Toluene            | 306(19.6)        | 748(47.8)                |
| 6) Benzene            | 304(19.8)        | 792(51.9)                |

\*\*COD values determined using a Friedrich's condenser

\*COD values determined using a dry ice condenser filled with crushed ice-water mixture

\*\*\*Sodium stearate's low value appears to result partially from incomplete oxidation

TABLE 7. CARBON CONTENT OF STOCK SAMPLE SOLUTIONS USING  
TOTAL CARBON ANALYZER

| Organic Compound  | Carbon Taken, mg/l | Carbon Found, mg/l | % Error |
|-------------------|--------------------|--------------------|---------|
| Formaldehyde      | 200.0              | 193.9              | 3.1     |
| Benzene           | 461.0              | 451.4              | 2.1     |
| Toluene           | 456.0              | 448.1              | 1.7     |
| Acetic Acid       | 200.0              | 192.1              | 4.0     |
| Sucrose           | 210.3              | 205.7              | 2.3     |
| Ethyl Alcohol     | 260.8              | 269.3              | 3.0     |
| Oleic Acid        | 382.9              | 390.6              | 2.0     |
| T-butyl Alcohol   | 324                | 317.8              | 2.0     |
| 3-Hydroxypyridine | 316                | 308.4              | 2.3     |
| Lactic Acid       | 200                | 207.0              | 4.0     |
| Pyridine          | 380                | 385.2              | 1.5     |



TABLE 1. EFFECT OF SOLAR RADIATION BEING STORED WITHIN THE  
SOLAR RADIATION STORAGE SYSTEM

| Compound          | Volume of Silver Sulfate Solution<br>200 ml, 10% (V of Recovery) |            |            |            |            |            |            |            |    |    |
|-------------------|------------------------------------------------------------------|------------|------------|------------|------------|------------|------------|------------|----|----|
|                   | 2                                                                | 5          | 10         | 15         | 20         | 25         | 30         | 35         | 40 | 45 |
| Acetic acid       | 28.3(53.1)                                                       | 31.5(59.1) | 33.8(62.2) | 35.5(66.6) | 37.7(70.7) | 45.6(85.5) | 51.8(97.1) | 52.2(98.0) |    |    |
| Benzene           | 19.4(37.6)                                                       | 13.7(8.9)  | 12.2(8.3)  | 6.5(4.8)   | 14.8(9.1)  | 10.8(6.5)  | 75.5(49.1) | 66.1(43.2) |    |    |
| Benzoic acid      | 51.1(91.8)                                                       | 68.5(96.6) | 65.6(98.6) | 68.3(92.7) | 71.9(95.4) | 76.9(97.7) | 76.7(99.1) | 77.4(99.7) |    |    |
| Ethyl alcohol     | 26.8(35.3)                                                       | 40.8(77.4) | 67.8(96.1) | 98.8(98.8) | 93.4(98.5) | 95.9(98.8) | 98.2(99.1) | 98.5(99.4) |    |    |
| Formic acid       | 34.8(65.3)                                                       | 37.9(69.4) | 36.4(68.3) | 31.5(58.1) | 37.7(70.7) | 33.8(61.9) | 51.8(97.2) | 47.2(88.6) |    |    |
| Hydrochloric acid | 63.2(85.9)                                                       | 66.6(88.1) | 66.6(87.1) | 68.9(91.4) | 91.2(95.2) | 93.3(96.3) | 94.8(97.1) | 99.8(99.1) |    |    |
| Lactic acid       | 64.8(82.5)                                                       | 45.6(65.5) | 47.6(68.3) | 47.4(68.7) | 49.8(70.8) | 51.6(76.8) | 51.8(97.1) | 51.9(97.3) |    |    |
| Maleic acid       | 38.1(58.9)                                                       | 13.3(9.2)  | 11.2(7.7)  | 29.2(28.2) | 19.8(13.7) | 46.8(52.4) | 26.9(29.6) | 33.9(33.4) |    |    |
| Pyridine          | 1.8(1.6)                                                         | 0.8(0.6)   | 0.9(0.7)   | 1.2(0.8)   | 1.5(1.2)   | 9.2(7.2)   | 12.9(11.8) | 14.9(11.3) |    |    |
| Sucrose           | 48.1(87.5)                                                       | 51.2(96.4) | 52.4(98.4) | 58.1(98.3) | 58.4(98.9) | 58.7(98.4) | 52.2(93.8) | 51.6(95.5) |    |    |
| Toluene           | 51.5(94.2)                                                       | 42.3(27.8) | 34.8(25.3) | 10.9(7.8)  | 12.4(7.9)  | 7.3(4.7)   | 28.8(13.3) | 14.5(9.3)  |    |    |

TABLE III. EFFECT OF DIFFERENT CALCULATIONS ON CRO VALUES FOR DIFFERENT ORGANIC COMPOUNDS

| Compound           | $GL_2(SR_1)_3$ | $C_{200}_0$ | CRO Values, $mg/l$ (2 of Recovery) | $Fe_2(SR_1)_3$ | $2-CRO_0$   |
|--------------------|----------------|-------------|------------------------------------|----------------|-------------|
| Acetic acid        | 10.2(10.8)     | 6.3( 11.4)  | 1.0(15.6)                          | 2.0( 3.8)      | 5.2( 9.8)   |
| Benzene            | 20.2(13.1)     | 11.8( 7.2)  | 25.5(26.6)                         | 27.9(28.1)     | 12.0( 7.8)  |
| tert-Butyl alcohol | 60.6(46.7)     | 61.0( 47.0) | 59.0(45.5)                         | 48.1(37.1)     | 54.0( 41.6) |
| Butyl alcohol      | 51.5(48.4)     | 20.5( 19.6) | 52.3(50.1)                         | 48.3(46.0)     | 30.0( 20.8) |
| Benzaldehyde       | 36.0(17.4)     | 41.0( 76.9) | 35.5(85.9)                         | 35.2(85.9)     | 48.0( 90.0) |
| 3-Pentadecapentene | 74.3(76.7)     | 97.0(100.2) | 76.4(70.9)                         | 76.0(70.5)     | -           |
| Lactic acid        | 41.6(70.0)     | 43.0( 80.6) | 41.6(70.0)                         | 25.5(47.8)     | 52.5( 96.6) |
| Malic acid         | 75.5(17.6)     | 20.0(19.6)  | 10.1( 7.0)                         | 39.6(27.6)     | 32.0( 22.7) |
| Pyridine           | 0.0( 0.6)      | 0           | 2.0( 1.6)                          | .40(3.2)       | 5.2( 4.1)   |
| Sucrose            | 51.7(50.2)     | -           | 52.5(93.6)                         | 51.7(92.2)     | 66.0(101.5) |
| Valerone           | 64.4(20.6)     | 33.0(21.0)  | 19.8(12.7)                         | 25.1(16.0)     | 36.0( 35.0) |

TABLE II. EFFECT OF COMBINING CATALYSTS ON ISO YIELDS  
FOR DIVERSE ORGANIC COMPOUNDS

| Compounds          | 200 Vol.-%, 100/1 (2 of Secondary)                    |                                              |                                                           |                                                                                           |                                                                                           |
|--------------------|-------------------------------------------------------|----------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
|                    | $\text{Al}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4$ | $\text{Al}_2(\text{SO}_4)_3 + \text{CaSO}_4$ | $\text{Al}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{SO}_4)_3$ | $\text{Al}_2(\text{SO}_4)_3 + \frac{\text{Al}_2(\text{SO}_4)_3}{2\text{Na}_2\text{SO}_4}$ | $\text{Fe}_2(\text{SO}_4)_3 + \frac{\text{Fe}_2(\text{SO}_4)_3}{2\text{Na}_2\text{SO}_4}$ |
| Acetic acid        | 29.6(15.5)                                            | 8.5( 15.6)                                   | 8.4(15.8)                                                 | 7.0(13.1)                                                                                 | 9.2( 17.3)                                                                                |
| Benzene            | 46.8(38.4)                                            | 6.4( 4.2)                                    | 17.4(11.3)                                                | 5.5( 3.6)                                                                                 | 12.0( 7.8)                                                                                |
| tert-Butyl alcohol | 79.2(81.2)                                            | 29.0( 21.3)                                  | 49.4(28.2)                                                | 36.1(26.3)                                                                                | 74.8( 57.7)                                                                               |
| 2-hpt. alcohol     | 95.6(53.3)                                            | 31.0( 29.7)                                  | 51.5(40.6)                                                | 40.5(28.8)                                                                                | 76.0( 72.0)                                                                               |
| Formaldehyde       | 62.0(78.8)                                            | 42.0( 78.8)                                  | 38.8(72.8)                                                | 37.3(70.0)                                                                                | 55.2(103.3)                                                                               |
| 3-hpt-methylolone  | 57.2(79.7)                                            | 107 (110.5)                                  | 78.0(80.5)                                                | - - -                                                                                     | - - -                                                                                     |
| Lactic acid        | 45.6(35.5)                                            | 31.0( 58.1)                                  | 36.4(88.2)                                                | 45.0(84.4)                                                                                | 55.6(104.2)                                                                               |
| Glucic acid        | 31.2(21.6)                                            | 46.0( 31.8)                                  | 24.8(17.2)                                                | 28.2(18.5)                                                                                | 54.2( 37.5)                                                                               |
| Pyridine           | 6.0( 5.40)                                            | 3.1( 2.4)                                    | 5.6( 4.4)                                                 | 1.4( 1.1)                                                                                 | 4.0( 3.8)                                                                                 |
| Sucrose            | 51.2(54.3)                                            | 61.0(100.6)                                  | 56.1( 100)                                                | 54.3(26.7)                                                                                | - - -                                                                                     |
| Toluene            | 50.4(31.2)                                            | 3.7( 2.4)                                    | 36.4(10.5)                                                | 7.8( 5.0)                                                                                 | 38.0( 26.3)                                                                               |

TABLE II (continued)

| Compound           | C20 Values, mg/l. (S of Recovery)                                         |                                              |                                              |                                              |                                 |
|--------------------|---------------------------------------------------------------------------|----------------------------------------------|----------------------------------------------|----------------------------------------------|---------------------------------|
|                    | $\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2(\text{SO}_4)_3 + \text{CaSO}_4$ | $\text{Fe}_2(\text{SO}_4)_3 + \text{CaSO}_4$ | $\text{Fe}_2(\text{SO}_4)_3 + \text{CaSO}_4$ | $\text{Fe}_2(\text{SO}_4)_3 + \text{CaSO}_4$ | $\text{CaSO}_4 + \text{CaSO}_4$ |
| Acetic acid        | 7.0(13.1)                                                                 | 8.7( 16.3)                                   | 7.5( 14.0)                                   | 6.0( 11.3)                                   | 11.4( 23.3)                     |
| Benzene            | 10.5( 6.8)                                                                | 6.1( 2.7)                                    | 5.0( 3.2)                                    | 6.0( 4.0)                                    | 6.3( 2.8)                       |
| tert-Butyl alcohol | 48.3(38.0)                                                                | 37.5( 29.0)                                  | 31.3( 24.1)                                  | 39.6( 30.5)                                  | 31.0( 26.0)                     |
| Ethyl alcohol      | 52.7(38.5)                                                                | 36.0( 36.5)                                  | 33.0( 31.6)                                  | 38.0( 36.4)                                  | 37.0( 35.5)                     |
| Formaldehyde       | 35.8(33.4)                                                                | 45.0( 81.6)                                  | 46.0( 86.3)                                  | 42.0( 80.3)                                  | 33.0( 62.0)                     |
| 3-Hydroxypropylene | 71.0(74.1)                                                                | -                                            | 96.0( 99.1)                                  | -                                            | 102.0(105.3)                    |
| Lactic acid        | 32.2(88.4)                                                                | 53.0( 99.4)                                  | 37.0( 69.4)                                  | 40.0( 75.0)                                  | 36.0( 67.5)                     |
| Oxalic acid        | 32.6(22.5)                                                                | 47.0( 38.5)                                  | 27.0( 18.7)                                  | 23.6( 16.3)                                  | 42.0( 29.0)                     |
| Pyridine           | 5.1(6.00)                                                                 | 3.0( 2.4)                                    | 2.0( 1.6)                                    | 0                                            | 2.4( 2.0)                       |
| Sucrose            | 36.6(25.7)                                                                | 60.5(87.8)                                   | 63.0(117.2)                                  | 59.2(105.5)                                  | 58.0(105.3)                     |
| Toluene            | 32.4( 7.8)                                                                | 10.0( 6.4)                                   | 8.5( 5.4)                                    | 5.6( 3.6)                                    | 5.1( 3.2)                       |

TABLE 112. EFFECT OF SULFUR SULFATE ON CSD VALUES IN THE  
PRESENCE OF ALIPHATIC AND AROMATIC SULFATES

| Compound             | Volume of Sulfur Sulfate Solution<br>(CSD Volume, ml) (% of Recovery) |            |            |            |             |             |             |
|----------------------|-----------------------------------------------------------------------|------------|------------|------------|-------------|-------------|-------------|
|                      | 0                                                                     | 5          | 10         | 15         | 20          | 25          | 30          |
| Acetic<br>acid       | 29.6(55.5)                                                            | 35.6(66.8) | 38.9(74.5) | 44.0(82.6) | 46.0(86.3)  | 50.1(93.9)  | 50.8(95.3)  |
| Benzoic<br>acid      | 46.8(30.4)                                                            | 41.5(27.0) | 50.1(32.6) | 58.4(38.8) | 56.6(35.5)  | 66.1(43.6)  | 71.2(46.3)  |
| Benzoic<br>alcohol   | 79.2(61.8)                                                            | 85.0(65.5) | 98.4(68.2) | 91.9(71.8) | 98.5(73.96) | 103.1(77.2) | 107.9(83.2) |
| Butyl<br>alcohol     | 55.6(57.3)                                                            | 66.4(68.0) | 67.1(69.3) | 95.0(91.8) | 96.1(90.2)  | 98.4(94.3)  | 95.6(91.6)  |
| Benzoic<br>alcohol   | 42.8(77.8)                                                            | 43.2(80.9) | 42.5(77.9) | 42.9(80.6) | 48.2(90.6)  | 51.7(97.3)  | 52.7(98.1)  |
| 3-Ethoxy-<br>butanol | 77.2(79.7)                                                            | 79.1(81.7) | 80.3(82.9) | 86.4(89.2) | 86.9(89.7)  | 90.1(93.1)  | 95.0(98.1)  |
| Isobutyric<br>acid   | 45.6(85.5)                                                            | 47.2(88.5) | 47.0(88.1) | 48.2(90.4) | 49.3(93.6)  | 51.1(95.9)  | 52.5(98.4)  |
| Glacetic<br>acid     | 31.2(21.6)                                                            | 38.9(23.1) | 47.4(27.0) | 51.5(27.8) | 57.5(29.0)  | 51.3(25.5)  | 43.1(23.8)  |
| Pyridine             | 6.8( 5.4)                                                             | 7.0( 5.3)  | 7.2( 5.7)  | 7.4( 5.9)  | 7.9( 6.2)   | 8.7( 7.0)   | 9.5( 7.5)   |
| Succinic<br>acid     | 51.2(31.3)                                                            | 51.7(32.2) | 52.4(33.4) | 53.3(35.0) | 53.8(35.4)  | 53.5(35.4)  | 54.0(36.3)  |
| Toluene              | 50.4(32.2)                                                            | 51.5(32.9) | 52.0(33.7) | 54.5(34.8) | 56.4(37.3)  | 69.2(44.2)  | 76.7(49.0)  |

TABLE 13. THE EFFECT OF DIFFERENT CATALYST OR CATALYST  
COMBINATIONS ON COD FOR ACETIC ACID

| Catalyst                                                                                      | COD, mg/l (% of Recovery) |
|-----------------------------------------------------------------------------------------------|---------------------------|
| 1g $\text{Al}_2(\text{SO}_4)_3$                                                               | 10.0(18.8)                |
| 1g $\text{HgSO}_4$                                                                            | 8.0(15.0)                 |
| 1g $\text{HgSO}_4$ + 1g $\text{Al}_2(\text{SO}_4)_3$                                          | 29.6(55.9)                |
| 1g $\text{HgSO}_4$ + 1g $\text{Al}_2(\text{SO}_4)_3$ + 5 ml $\text{Ag}_2\text{SO}_4$ Solution | 35.6(66.8)                |
| 1g $\text{HgSO}_4$ + 1g $\text{Al}_2(\text{SO}_4)_3$ + 10 ml $\text{Ag}_2\text{SO}_4$ "       | 39.9(74.9)                |
| 1g $\text{HgSO}_4$ + 1g $\text{Al}_2(\text{SO}_4)_3$ + 15 ml $\text{Ag}_2\text{SO}_4$ "       | 44.0(82.6)                |
| 1g $\text{HgSO}_4$ + 1g $\text{Al}_2(\text{SO}_4)_3$ + 20 ml $\text{Ag}_2\text{SO}_4$ "       | 46.0(86.3)                |
| 1g $\text{HgSO}_4$ + 1g $\text{Al}_2(\text{SO}_4)_3$ + 50 ml $\text{Ag}_2\text{SO}_4$ "       | 50.8(95.3)                |
| 1g $\text{HgSO}_4$ + 1g $\text{Al}_2(\text{SO}_4)_3$ + 70 ml $\text{Ag}_2\text{SO}_4$ "       | 51.5(96.6)                |

TABLE 14. STANDARD METHOD VS. REVISED METHOD USING  
HOUSTON AREA WATER SAMPLES

| Sample Site Location                              | Mean COD, mg/l  |                | Revised Method<br>Standard Method<br>X100 |
|---------------------------------------------------|-----------------|----------------|-------------------------------------------|
|                                                   | Standard Method | Revised Method |                                           |
| 1 - Buffalo Bayou-Franklin<br>at U.S. Post Office | 34.0            | 45.6           | 134                                       |
| 2 - Allen's Landing at Main                       | 36.8            | 58.4           | 108                                       |
| 3 - First Southwest Downfall                      | 30.4            | 58.0           | 284                                       |
| 4 - Buffalo Bayou at Eastern<br>Freeway           | 30.8            | 49.9           | 161                                       |
| 5 - Brown & Root                                  | 32.0            | 34.6           | 108                                       |
| 6 - Buffalo Bayou at Lockwood                     | 40.8            | 50.6           | 124                                       |
| 7 - Northside Sewage Treatment<br>Plant           | 89.6            | 69.6           | 78                                        |
| 8 - Ship Channel Turning Basin                    | 95.6            | 105.9          | 110                                       |
| 9 - 610 Bridge                                    | 116.4           | 146.8          | 124                                       |
| 10 - Sims Bayou at Ship Channel                   | 99.6            | 190.4          | 191                                       |
| 11 - Oline Downfall #1 on Ship<br>Channel         | 135.2           | 135.6          | 119                                       |
| 12 - Bouy #139 in Ship Channel                    | 152.4           | 164.45         | 108                                       |
|                                                   |                 | Av.            | 131                                       |